ESR studies of doping C_{60} fullerene by zinc, cadmium, copper, gallium, and indium vapors

S. P. Solodovnikov

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: 007 (095) 135 5085

In the ESR spectra recorded at the beginning of the doping reaction of C_{60} fullerene by zinc, gallium, and indium vapors, signals corresponding to C_{60}^- were observed. In the course of reduction, these signals disappeared and reversibly transformed into the signals of higher charged C_{60}^{n-} anions. In the case of cadmium and copper, only the spectra of C_{60}^{n-} were recorded.

Key words: fullerene; ESR; conductivity.

The detection of conductivity and superconductivity in potassium and rubidium C_{60} fullerenides[1] gave impetus to the search for and studies of fullerenides of other metals.[2]

The major procedure for the preparation of fullerenides of alkali metals is vapor-phase synthesis, namely, the reaction of a metal vapor with solid C_{60}. Because the volatilities of other metals are small, a substantial increase in the temperature is necessary for this reaction to proceed with these metals. Presently, alternative liquid-phase reactions do not find wide use.[3,4]

ESR spectral study of the doping reaction of C_{60} fullerene by potassium demonstrated that at the beginning of the reaction, the spectra of the primary fullerenides KC_{60} and K_2C_{60} appeared, and then the spectra of the semiconducting K_xC_{60} phase ($x < 3$) and the conducting K_3C_{60} phase were recorded.[5] In the case of sodium fullerenides, the ESR spectra of the conducting phase were not observed.

The most typical spectrum was observed in the case of the primary fullerenides of alkali metals $M^+C_{60}^-$. This spectrum is characterized by a somewhat smaller value of the g factor compared to that of the free electron and by a sharp temperature dependence of the line width.[6] The line width decreases, and the amplitude of the signal increases by several times as the temperature decreases. Apparently, this characteristic feature is determined by the spherical symmetry of the radical anion and, as a result, by the dynamic Jahn—Teller effect.

It is reasonable to expect that $M^+C_{60}^-$ would form at the beginning of the reaction of alkali metals with C_{60}, whereas in the case of polyvalent metals, the one-electron stage does not necessarily occur.

When the thermodynamics of the formation of potassium fullerenides was discussed, it was noted that the K_3C_{60} phase is more stable than the K_2C_{60} and KC_{60} phases due to a higher energy of electrostatic interactions between ions in the crystal lattice.[7] In consequence of these energy relations, disproportionation occurs

$$KC_{60} + K_2C_{60} \rightarrow K_3C_{60} + C_{60},$$

which manifests itself as a change in the relative intensities of ESR lines of these fullerenides upon annealing.[5] Therefore, the kinetics of the heterogeneous reaction of the formation of potassium fullerenides is not determined exclusively by the redox potentials of fullerene and potassium.

The aim of this work is to prepare new fullerenides and to study the characteristic features of their formation. The occurrence of C_{60}^- radical anions or their absence in the case of the use of polyvalent metals may provide valuable data on the character of redox reactions between reagents and on the effect of electrostatic interactions between ions on the formation of particular fullerenides.

Experimental

Metal fullerenides were prepared in ESR tubes. C_{60} fullerene (1—2 mg) and excess metal were used in the reaction. Zinc, gallium, and indium were used as pieces. Cadmium and copper were used as powders. The samples in tubes were evacuated to 10^{-3}—10^{-4} Torr at 300 °C for 2—3 h. Then the tubes were sealed off and placed in a cylindrical furnace (500 °C). The ESR spectra were recorded on a Varian E-12 spectrometer at 300 or 77 K at specified intervals. The reaction time was varied from 18 to 48 h depending on the metal. The reversibility of the reaction of the formation of fullerenides was studied in the mode such that one end of the tube containing M_xC_{60} was kept at 500 °C and the larger part of the tube was kept at room temperature.

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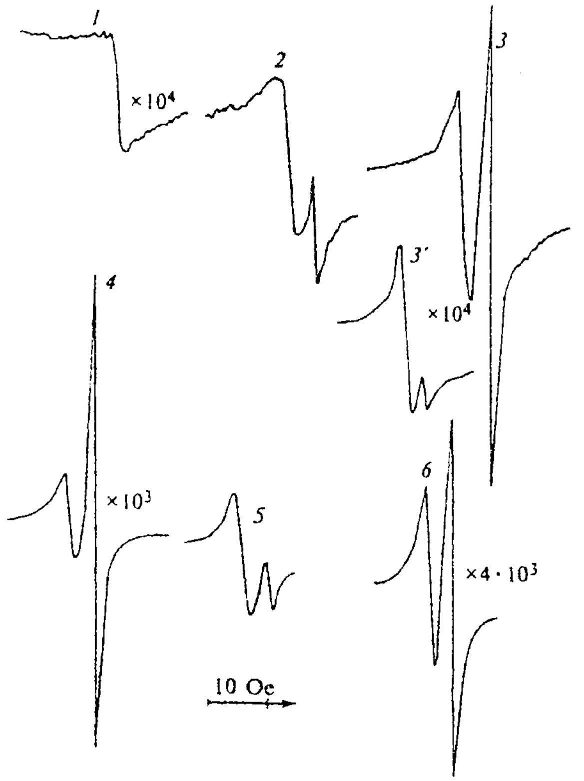

Fig. 1. ESR spectra of Zn_xC_{60} at 77 K (*1—3*, *4—6*) and 300 K (*3'*). The amplitude modulation of the magnetic field was 1 Oe, (spectra *1—4*, *6*) or 2.5 Oe (spectrum *5*); before the beginning (*1*), the reaction time (h): after 2 (*2*), 5 (*3*), 22 (*4*), and 48 (*5*); of the reaction and after 1 h of the reverse reaction (*6*).

Results and Discussion

In the case of Zn (48 h), Ga (22 h), and In (18 h), duration of doping was determined by the kinetics of accumulation and consumption of C_{60}^-. The ESR spectra of Zn_xC_{60} at different stages of the reaction are shown in Fig. 1.

The spectrum *1*, which was recorded after evacuation at 300 °C, corresponds to localized paramagnetic centers C_{60}. The number of these centers is of the order of 10^{19} per mole of C_{60}.[4]

The intensity of the signal of C_{60}^- (the line in the strong field) in the spectra *2—5* passes through a maximum. The spectra *3* and *3'* reflect the temperature dependence of the amplitude of the signal of C_{60}^-. The spectrum *6* was recorded after heating Zn_xC_{60} at 500 °C for 1 h with the temperature gradient that is necessary for the decomposition of fullerenides to proceed.

The signal in the weak field (the spectra *2—6*) has a more complex nature. In the spectra *2* and *3*, this signal is a superposition of lines of localized paramagnetic centers C_{60} and products of the further reduction of C_{60}^-. These products can form a semiconducting phase.[5] In the spectra *4—6*, the line in the weak field corresponds to products of the reduction of C_{60}^-, which is confirmed by the reverse reaction characterized by the spectrum *6*. An increase in the intensity of the signal of C_{60}^- in the spectrum *6* compared to the spectrum *5* is associated with the reverse reaction:

$$C_{60}^{n-} \rightarrow C_{60}^- + (n-1)e.$$

The electrons that are detached are bound by zinc cations. Zinc atoms that formed were absorbed on the cold part of the tube as a metallic mirror. The reaction is reversible, which indicates that products of the reduction are stable under rather drastic conditions of doping.

At the initial stage, spectral changes that occur in the course of the doping reaction of C_{60} by gallium or indium are similar to those described above. Reduction by indium proceeded somewhat faster than reduction by gallium. The signal virtually disappeared at the end of doping. An analogous situation was observed in the doping reaction by potassium: when the K_3C_{60} conducting phase formed, the line width sharply increased, and the amplitude of the signal decreased. When K_6C_{60} formed, the sample became virtually diamagnetic.[5]

Decomposition of Ga_xC_{60} and In_xC_{60} (40 min) resulted in the appearance of a spectrum in which the C_{60}^{n-} and C_{60}^- lines occur. This indicates that the deep reduction is reversible, and higher anions are stable.

The spectra of the product of doping by cadmium (18 h) and copper (28 h) do not contain lines of the initial C_{60}^- radical anion. The intensity of an ESR signal assigned to C_{60}^{n-} anions increased with time. After doping by copper for 14 h, this signal reached the maximum. This signal decreased by a factor of 7 at the end of doping. When the reverse reaction was carried out (1.5 h), the signal again increased by an order of magnitude. An analogous situation was observed in the doping by cadmium.

Our results suggest two types of reactions of polyvalent metals with fullerene:

$$M^{(n)} + nC_{60} \rightarrow M^{n+}nC_{60}^- \text{ and } M^{(n)} + C_{60} \rightarrow M^{n+}C_{60}^{n-},$$

where n is the valence.

Based on our data, the former reaction occurs in the case of Na, K, Mg, Zn, Ga, and In, and the latter reaction occurs in the case of Cd, Cu, and Hg.[4,5]

The high stability of C_{60}^{n-} anions at 500 °C, which we observed, provides evidence that other metals can be used in the synthesis of fullerenides.

We have obtained new fullerenides of metals (Zn, Ga, In, Cd, and Cu) and studied the characteristic features of their formation.

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